

X-ray Fluorescence: EDXRF vs WDXRF

Introduction: In an effort to save money, space, sample preparation time, or simply to add an analytical instrument to their process many companies will decide to evaluate energy dispersive x-ray fluorescence (EDXRF) analyzers as a substitute for their standard wavelength dispersive x-ray fluorescence (WDXRF) analysis. This is very common with geological applications where WDX is the benchmark, but it occurs with many other applications as well. What all these companies eventually discover is that EDXRF is not the low cost drop in replacement that they thought it would be but has significant differences, some positive and some negative, that must be considered in the evaluation process or else dealt with later when it may be less convenient.

As most scientifically minded persons know, the energy of the light photon increases as the wavelength decreases, so in an EDX spectra the low atomic number elements are on the left while they are to the right of a WDX spectra. But the difference goes far beyond that.

WDXRF: The WDXRF analyzer uses a x-ray source to excite a sample. X-rays that have wavelengths that are characteristic to the elements within the sample are emitted and they along with scattered source x-rays go in all directions. A crystal or other diffraction device is placed in the way of the x-rays coming off the sample. A x-ray detector is positioned where it can detect the x-rays that are diffracted and scattered off the crystal. Depending on the spacing between the atoms of the crystal lattice (diffractive device) and its angle in relation to the sample and detector, specific wavelengths directed at the detector can be controlled. The angle can be changed in order to measure elements sequentially, or multiple crystals and detectors may be arrayed around a sample for simultaneous analysis.

EDXRF: The EDXRF analyzer also uses an x-ray source to excite the sample but it may be configured in one of two ways. The first way is direct excitation where the x-ray beam is pointed directly at the sample. Filter made of various elements may be placed between the source and sample to increase the excitation of the element of interest or reduce the background in the region of interest. The second way uses a secondary target, where the source points at the target, the target element is excited and fluoresces, and then the target fluorescence is used to excite the sample. A detector is positioned to measure the fluorescent and scattered x-rays from the sample and a multichannel analyzer and software assigns each detector pulse an energy value thus producing a spectrum. Note that there is absolutely no reason why the spectra cannot be displayed in a wavelength dependent graph format.

Points of Comparison

1. Resolution: It describes the width of the spectra peaks. The lower the resolution number the more easily an elemental line is distinguished from other nearby x-ray line intensities.

a. The resolution of the WDX system is dependent on the crystal and optics design,

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particularly collimation, spacing and positional reproducibility. The effective resolution of a WDX system may vary from 20 eV in an inexpensive benchtop to 5 eV or less in a laboratory instrument. The resolution is not detector dependent.

b. The resolution of the EDX system is dependent on the resolution of the detector. This can vary from 150 eV or less for a liquid nitrogen cooled Si(Li) detector, 150-220 eV for various solid state detectors, or 600 eV or more for gas filled proportional counter.

ADVANTAGE WDXRF: High resolution means fewer spectral overlaps and lower background intensities.

ADVANTAGE EDXRF: WDX crystal and optics are expensive, and are one more failure mode.

2. Spectral Overlaps: Spectral deconvolutions are necessary for determining net intensities when two spectral lines overlap because the resolution is too high for them to be measured independently.

a. With a WDX instrument with very high resolution (low number of eV) spectral overlap corrections are not required for a vast majority of elements and applications. The gross intensities for each element can be determined in a single acquisition.

b. The EDXRF analyzer is designed to detect a group of elements all at once. The some type of deconvolution method must be used to correct for spectral overlaps. Overlaps are less of a problem with 150+ eV resolution systems, but are significant when compared to WDXRF. Spectral overlaps become more problematic at lower resolutions.

3. Background: The background radiation is one limiting factor for determining detection limits, repeatability, and reproducibility.

a. Since a WDX instrument usually uses direct radiation flux the background in the region of interest is directly related to the amount of continuum radiation within the region of interest the width of which is determined by the resolution.

b. The EDXRF instrument uses filters and/or targets to reduce the amount of continuum radiation in the region of interest which is also resolution dependent, while producing a higher intensity x-ray peak to excite the element of interest.

Even - WDX has an advantage due to resolution. If a peak is one tenth as wide it has one tenth the background.

EDX counters with filters and targets that can reduce the background intensities by a factor of ten or more.

4. Source Efficiency: How efficiently the source x-rays are utilized determines how much power is needed to make the system work optimally. Higher power costs much more money.

a. Every time an x-ray beam is scattered off a surface the intensity is reduced by a factor of 100 or so. For any XRF system intensity is lost in the process of exciting the sample, but a WDX analyzer also loses a factor of 100 in intensity at the diffraction device, although some modern multilayers are more efficient. The sample to detector path length is often 10 cm or more introducing huge geometrical

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losses.

b. With direct excitation the EDX system avoids wasting x-ray intensity. When filters are used the 3 to 10 times more energy is required, and when secondary targets are used 100 times more energy is required making the total energy budget similar between Secondary target EDX and WDX systems before the path length is considered. An EDX system typically has sample to detector path lengths less than 1 cm.

ADVANTAGE EDXRF: In order to achieve similar counts at the detector a WDX system needs 100-1000 times the flux of a direct excitation EDX system and 10-100 times the flux of a secondary target system. This one principle reason WDX systems cost more.

5. **Excitation Efficiency** : Usually expressed in PPM per count-per-second (cps) or similar units, this is the other main factor for determining detection limits, repeatability, and reproducibility. The relative excitation efficiency is improved by having more source x-rays closer to but above the absorption edge energy for the element of interest.

a. WDXRF generally uses direct unaltered x-ray excitation, which contains a continuum of energies with most of them not optimal for exciting the element of interest.

b. EDXRF analyzers may use filter to reduce the continuum energies at the elemental lines, and effectively increasing the percentage of x-rays above the element absorption edge. Filters may also be used to give a filter fluorescence line immediately above the absorption edge, to further improve excitation efficiency. Secondary targets provide an almost monochromatic line source that can be optimized for the element of interest to achieve optimal excitation efficiency.